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BIOMOLECULAR EVIDENCE FOR THE FORMATION OF AN EXTENSIVE TAR LAYER GENERATED DURING A VOLCANIC EVENT ON MONTSERRAT

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The island of Montserrat comprises four volcanic centres of which only the Soufrière Hills, at over 900 m, remains active (Harford et al., 2002). On 26th December 1997 a volcanic event occurred where the flank rocks of the edifice and dome talus on the south-western side failed, due to hydrothermal weakening of the edifice rocks. A subsequent blast generated a pyroclastic density current (PDC) that covered and devastated 10 km^2 of southern Montserrat and of the area was covered by a black 'tar' layer of 1-4 mm thick. Investigation of the layer indicated that the tar formed over a surface that had been already striated and grooved prior to deposition and it was postulated that a cloud of heated organic material had combusted to form the tar layer nearly synchronously as the hot current inundated the area (Sparks et al., 2002). This investigation tested the above hypothesis through comparative analyses of organic compounds (both molecular and macromolecular) extant in the tar and its putative sources, i.e. the local vegetation (grass) and soil.

The major biomolecular components of the tar were isolated then analysed by GC and GC/MS, classes investigated included: lipids (hydrocarbons, *n*-alkanols, *n*-alkanoic acids, sterols), carbohydrates and lignin (CuO oxidation). Analysis of freely extractable lipids revealed that despite the high temperatures associated with the PDC a lipid signature, indicative of an origin from the grass *and* soil, was still extant within the tar layer. The distribution of major *n*-alkanes in the hydrocarbon fraction extracted from the tar correlated remarkably well with those of the vegetation and soil indicating that organic matter from one or both of these materials constituted an important fraction of this sample. Investigation of other functionalised acyclic lipids enabled additional clarification concerning the source of organic matter. The *n*-alkanol fraction derived from the tar exhibited a wide range of homologues as observed for the soil. However, the C_{22} and C_{32} homologues were present at a higher concentration, relative to the peripheral components, than observed in the soil thereby indicating that there had also been a contribution from the grass.

Application of ^{13}C CP/MAS NMR corroborated findings obtained from the molecular analyses. The spectra obtained for tar MVO342 exhibited a large aromatic signal that maximised at 128 ppm in contrast to the grass and soil which generated a predominant O-alkyl signal mainly attributable to carbohydrates (76842 and 3874 mg^{-1}_{TOC} total hydrolysable carbohydrates, respectively). This was indicative of naturally charred materials (Simpson and Hatcher, 2004) whilst the O-alkyl signal was greatly diminished paralleling the almost total loss of carbohydrates (93 mg^{-1}_{TOC}, total hydrolysable carbohydrates). Additionally, there was a much larger alkyl carbon component that correlated with the occurrence of a large unresolved complex mixture (UCM) in the hydrocarbon fraction of the sample. With an integral of over 50% the signal relating to aromatic carbon was even more dominant relative to other carbon environments in the spectra obtained for tar MVO662 thereby attesting to the even greater amount of thermal alteration that been undergone by this sample (Simpson and Hatcher, 2004).

These findings suggest that the organic matter constituting the tar had been heated in excess of 300°C, thereby correlating with additional reflectance data indicating minimum temperatures of 325-370ºC and up to 425ºC.

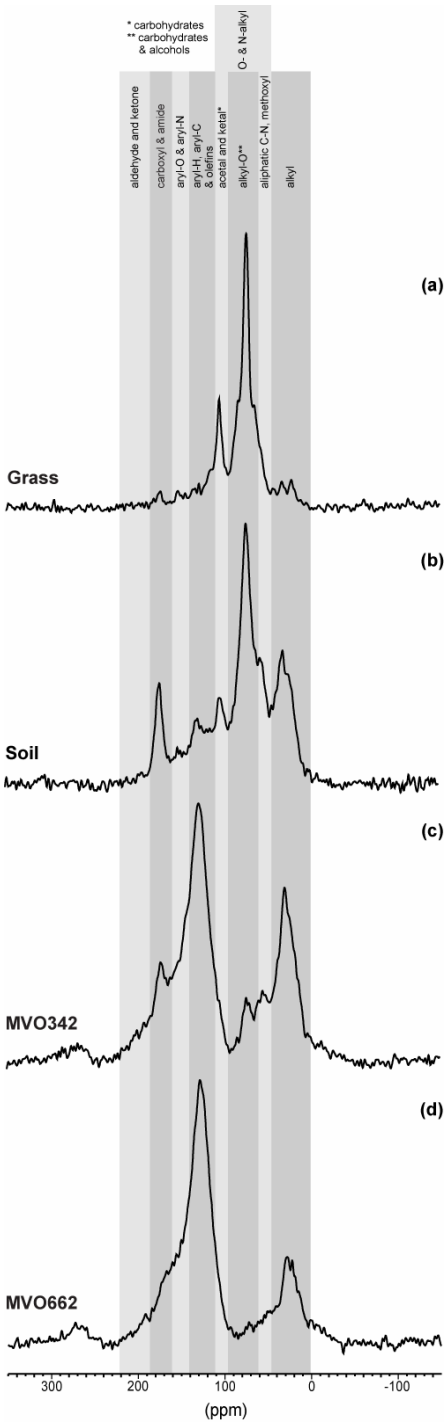

Figure 1. Solid state ^{13}C NMR spectra of (a) grass, (b) soil, (c) MVO342 and (d) MVO662

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